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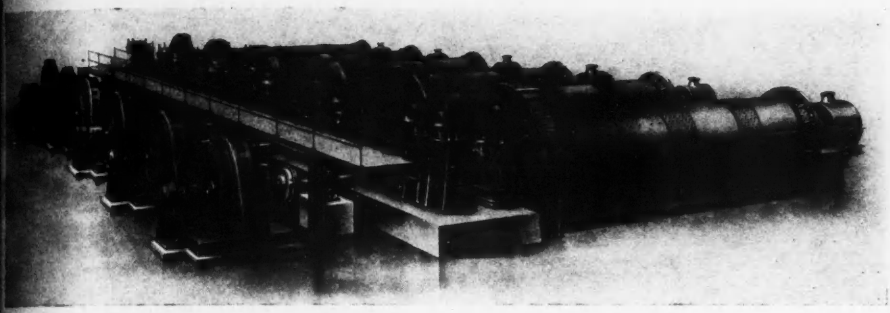

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Rotary Lime Kilns.

ADVANTAGES OF PULVERISED COAL FIRING.

After discussing the development of lime kilns and the methods of firing them, a writer in "Pit and Quarry" for September, 1940, says that the lime industry is undoubtedly entering a new era. Control of quality plus flexibility of production are the prime requisites, and pulverised coal as fuel seems to lend itself admirably to these requirements.

Power Requirements.—Generally speaking, the power requirements of any coal-pulverising equipment, which always includes a blower, will substantially exceed the power consumption of a gas-producer installation. Twenty kilowatts per ton of coal pulverised to a fineness of 90 per cent. through a 200-mesh sieve is a good figure at which to aim. This rate, however, is contingent on a Hardgrove grindability of 75 or better, and ample heat for mill drying up to 6 per cent. moisture in the coal must be available. Care should be taken not to allow load conservation to restrict the power reserve upon which depends the flexibility necessary when operating rates are increased by as much as 100 per cent. in a few hours. In older types of plants such a range is unheard of, but in more modern installations it is practised regularly with only a very slight efficiency drop.

Reliability.—In the older cement practice of pulverising coal during periods of off-peak demand for storage and later consumption an opportunity for regular inspection and repairs was afforded which simplified maintenance. However, in the direct-firing system the coal mill must be capable of continuous service for periods often exceeding six months.

Maintenance.—It is difficult to give coal-mill maintenance figures because of the difference in the grindability of coals. Some mills have required from 18 to 25 cents per ton of coal pulverised, which is prohibitive, whereas other mills function over periods of years for 2 to 3 cents per ton, which includes, not only grinding media, but all parts of the pulveriser subject to wear, fan and feeder included. In one case 75 Hardgrove bituminous coal was pulverised for a total replacement cost of between 0.5 and 0.75 cent per ton.

Coal Drying.—In no instances within the writer's knowledge have dryers been installed for the removal of moisture from the coal prior to milling. The reason for this is that the small quantity of coal to be pulverised can normally be dried in the mill by piping the primary air from a point about the discharge end of the kiln, where satisfactory temperatures are available. For reasons of safety coal-mill temperatures are limited to about 250 deg. F., and, to obtain accuracy of control, a damper for the admission of tempering air is always provided. Furthermore, temperature-control devices would be installed as a safeguard against carelessness on the part of the operator.

Most operators are familiar with the start-up period, when sufficient heat for drying the coal is not available from the kiln. The difficulties which ensue can be minimised by providing a bare space—the duct is usually insulated—in the hot-air pipe, where an air-induced coke fire or large kerosene torches can maintain a cherry-red temperature on the walls of the duct. Where city or natural gas is available, a torch inserted in the duct at a safe distance from the suction side of the mill is a help. There are a number of such aids in which the danger of fire is very remote because of the dampness of the coal. However, the necessity for using washed coal, which often carries moisture in excess of 12 per cent., presents an unusually difficult but not insurmountable problem. Increasing the temperature of the primary coal-carrying air is conducive to explosion. In such instances it is recommended that an insulated duct, equipped with expansion chambers or cyclones for dust removal, be installed so that the kiln-exit gases can be drawn to the coal mill. By this method it is possible, with the aid of a damper near the mill inlet, to obtain 8 or 9 per cent. CO_2 in the primary air, which will allow the use of temperatures substantially higher than would otherwise be permissible, and at the same time preclude the danger of explosion, because the quantity of CO_2 specified will not support combustion. The use of such a high percentage of CO_2 has no detrimental effect upon the flame. On the contrary, it will tend to lengthen and mellow it.

Coal-Mill Feeding.—One of the greatest advantages of the use of pulverised coal over other types of fuel is the accuracy in the control of kiln conditions which is made possible by modern feeding methods. At this point in the process there are many variables which tend to alter the rate of pulverising. For instance, in the most carefully designed feed bin there is likely to be segregation of coal. If the feeder is of the volumetric type, the changing of size from fine to coarse and *vice versa* will have a decided effect upon kiln conditions. Moisture in the coal may cause arching in the feed bin with an actual stoppage for a period

of time of the flow of coal to the feeder, which will result in a shortening of the flame with disturbing effect. Changing bin pressures usually have an upsetting effect, sometimes increasing or decreasing, as the case may be, the rate of feed. Constancy of coal feed is of utmost importance. Even when direct current is used for power in connection with volumetric, oscillating-pan, or table-type feeders there are too many variables present to allow the desired fineness of control. Not only must great accuracy accompany the feeding of coal to the mill, but flexibility is also essential if unvarying temperatures are to be maintained. The vibrating feeder is perfectly adapted to this work, being capable of an extremely broad range in the feed rate with a delicacy of control which is unequalled, and an accuracy which boasts of a variation tolerance of under 10 lb. when feeding at rates up to 8,000 lb. per hour. To ensure continuity of movement from the coal-feed chamber a vibrator should be attached to the side of the bin just above the point of exit. This will largely eliminate arching and will aid in maintaining a constant pressure of coal at the discharge point.

Coal Fineness.—Some authorities thought extreme fineness unnecessary, and gave as their reason a longer flame resulting from slower ignition of the coarse particles. The fact that the coarse particles usually dropped out of the air stream immediately upon leaving the coal pipe was supposed to make no difference, because the temperature of the lime into which it fell would be ample to complete the combustion and the heat derived therefrom would be very effective. This, however, was somewhat in error, because coke to contaminate the lime being discharged from the kiln invariably resulted. The other school of thought agreed that extreme fineness has a tendency to hasten combustion and shorten the flame, but thought there would be less possibility of lime discoloration by ash deposition and that a longer flame under better control could best be obtained through a deficiency of primary air, and it seems that the most satisfactory results have been obtained under this practice. The theoretical figure of 20 per cent. primary air is what most coal-pulverising equipment manufacturers have worked towards. There are some units, however, that require as much as 35 per cent. of the total air required for combustion to get the coal out of the mill. In such circumstances a short flame burning constantly against the coal pipe can be expected. On the other hand, with some types it is possible to force the coal into the kiln with as low as 12 per cent. on the primary side. This is the theoretical ideal which should, with other factors being equal, give the perfect flame. In this connection many of the coal companies have advocated high-volatile bituminous coal as being conducive to the longest flame, whereas the opposite usually proves to be correct in modern lime-burning, coals as low as 20 per cent. giving a much longer flame.

One of the strongest arguments favouring finely pulverised coal—90 to 95 per cent. passing the 200-mesh sieve—is its importance as a factor contributing to the formation of fire rings.

Coal Pipes.—Coal pipes correctly designed are of very great importance in the satisfactory use of pulverised coal as fuel. It is comparatively simple to

install the proper size of pipe to assist in obtaining the desired air velocities, and the theories concerning the advantages of different burners are numerous, but these features seem of minor value when compared with the advantages of coal piping constructed to give maximum practical flexibility. The decision of the operator to use ordinary iron pipe, a water-cooled nozzle, or an expensive chrome-nickel-steel burner must result from experience with local conditions, but it is best to obtain experienced advice concerning the possibilities of a flexible burner. By a flexible burner is meant one that can be quickly lengthened or shortened 5 ft. or 6 ft. with the least amount of help; that has an easy radial movement of at least 18 in. in all directions from the axis of the kiln; that can be removed and replaced with an interruption of less than half an hour. With such flexibility most of the variables encountered in the everyday operation of the kiln can be provided for, and a more accurate control of output is assured.

Fire Rings.—With the advent of pulverised coal as fuel the situation has become so acute that the success of the venture may be said to rest on this one point. Some operators who have installed pulverising mills are so concerned that they are considering other types of fuel or the removal of the mills altogether, while others, who are still using different types of equipment but who are convinced of the economy, flexibility and control features possible with pulverised coal, hesitate in making the change. To the question, "Can the formation of fire rings be eliminated or controlled," the answer is emphatically "Yes." A discussion of causes and corrective measures follows. It must necessarily be broad because it is a problem with many approaches.

Proper Sizing at the Feed End of the Kiln.—Most operators are staunch believers in feed uniformity, but for one reason or another do not practise it. They may give as their reasons inability to dispose of odd sizes, insufficient screening equipment, storage facilities unsuitable, wet screening, inability to dry properly or bad weather. If the urge to accomplish is strong enough, a method can, and must be, found if the difficulties are to be remedied. If it is dry screening, dry thoroughly and screen accurately. If it is wet screening, wash thoroughly and screen accurately.

Common practice is to divide the stone ranging from $\frac{1}{4}$ in. to $2\frac{1}{2}$ in. into two or three sizes and feed it to the kiln as such, whereas to obtain a thoroughly but mildly burned lime of the best quality, such a range should be broken into at least seven sizes. On the contrary, when a wide size range of stone is fed, the operators can expect the smaller ranges to be augmented by breakage occurring in the kiln, where two separate actions follow: (1) the thin, slabby pieces of stone will remain on the bottom of the charge, sliding on the lining with little chance of exposure to direct radiation; (2) the smaller sizes of cubical stone will form a perfect core in the centre of the rolling charge with little chance of absorbing heat either from direct radiation or transfer from the kiln lining. The inevitable result is overfiring in order to minimise the $CaCO_2$ always occurring in the small particles at the discharge end of the kiln. Overfiring carries penalties in the form of greater fuel consumption, lime discoloration, retarded slaking, faster settling

rate, reduced putty yield, and, last, but of major importance, it is conducive to the formation of fire rings.

In order to remove every trace of dust from the stone feed it has been common practice for a number of years to place a vibrating screen just ahead of the feed pipe, because it was believed that dust and extremely fine particles of material carried forward with the charge slagged to the lining at the hot point more readily than stone of normal size. This is true, but ordinarily the dust occurring at the feed point, if the prior screening has been fairly efficient, is rather small in quantity when compared with the breakage which takes place in the kiln after the charge has been exposed for the first time to the relatively high temperature of the feed end, more especially if several per cent. of moisture is present in the stone. This condition is naturally aggravated where heat exchangers are employed, and the added length of the newer kilns increases proportionately the tendency to great attrition. The French coefficient of the stone, as indicated by a Duval abrasion test, will give a fair indication of the normal breakage to be expected in the kiln. Therefore, the value of fine screening at the point of kiln entrance is questionable. The presence of a fairly great quantity of fine lime at the kiln exit—sometimes up to 25 per cent.—may present a marketing difficulty, but if the kiln is not overfired it need not be a cause of fire rings.

Impurities in the Kiln Feed.—The chief offenders in the formation of a fire ring are silica, iron and alumina. These are usually present in the limestone as well as the coal ash. By melting any of these three minerals in the pure state it will be found that very high temperatures will be required, much higher than those used in the dissociation of limestone. However, if a flux is added, they become sticky at approximately 2,450 deg. F., which is directly in the range of rotary-kiln flame temperatures. It is this stickiness which lays the foundation for an accumulation of the fine particles in the charge, which ultimately develops into a fire ring. Greater accuracy of feed sizing within closer limits will allow the reduction of calcining-zone temperatures to a range below the sticky point of the impurities, and fire rings will largely disappear.

Analysis of the Slag Ring.—An average analysis of fire-ring slag, formed while using a medium volatile coal from Central Pennsylvania, shows:—

	FIRE-RING SLAG	COAL ASH
SlO_2	9·36 per cent.	50·56 per cent.
Al_2O_3	4·18 ,, ,,	37·27 ,, ,,
Fe_2O_3	1·48 ,, ,,	4·32 ,, ,,
CaO	84·88 ,, ,,	2·68 ,, ,,
P_2O_5		0·69 ,, ,,
MgO		0·42 ,, ,,
SO_3		2·76 ,, ,,
Alkaline oxides		1·30 ,, ,,
Phosphorus in coal		0·015 ,, ,,

Dust in Primary and Secondary Air.—In many installations the kiln hood is the source of preheated primary air. This, it would seem, is the logical area

from which to obtain warm air for drying the coal in the mill because of its proximity. However, the kiln hood is usually a point of great air turbulence, because of the entrance of the secondary air through the discharging lime, the effect of which is likely to allow quantities of fine dust to be drawn into the warm-air duct. Whether the warm air is obtained from some point about the settling chamber at the feed end of the kiln or the hood, an expansion chamber or cyclone should be placed at a convenient point in the duct for the efficient removal of dust, because it is evident that the fine air-borne particles of lime are deposited directly on the sticky section, where they undoubtedly remain to increase the bulk of the fire ring.

In modern rotary-kiln practice the after-cooling of lime performs a dual service. Not only is the lime reduced to a temperature at which it can be handled and stored, but passage over the moving charge allows a substantial increase in air temperatures which lends itself advantageously in the drive for economy. But at the same time, in a number of instances, air velocities are great enough to allow the return of much very fine lime dust to the combustion area of the kiln, where it, too, joins in the formation of the fire ring. The fine particles thus deposited are the cause of the close-grained extremely hard fire rings that seem stubbornly to resist the best efforts at removal periods.

Flame Position.—As mentioned in a preceding paragraph, a flexible coal pipe can be of great assistance in placing the flame to the best advantage. Not only can the flame be placed directly on the lime charge, thereby lessening to some extent the tendency to superheat the brickwork at the point of impingement, but, by a longitudinal movement of the burner, the hot spot can be altered occasionally and the ring formation consequently allayed. This procedure, in conjunction with the use of coal containing approximately 20 lb. of ammonium sulphate per ton, will have the effect of loosening slag which has already formed. Thus, by regularly altering the hot point it is possible to loosen slag at one extremity while it is being formed at the other. It should be understood that the corrective and preventive measures suggested are based on the use of pulverised bituminous coal as fuel. Where fuel oil, petroleum coke, or natural gas is employed, troublesome slag rings are unknown.

Slag-Ring Prevention by the Use of a Basic Refractory.—Two rotary kilns, in which the formation of fire ring has been pronounced, are to have installed a section of magnesite lining backed by clay bricks at the normal point of ring formation. It is believed to be certain that the tendency toward slag formation at a rather well-defined section in the burning zone can be overcome, or at least reduced, by the use of a hard-burned low-iron magnesite brick. While magnesite linings take a good coating in service, the reaction produced between the magnesite and the charge is more refractory and would inevitably reduce the existing difficulties. Naturally, with magnesite laid directly against the shell of the kiln, there would be a much greater radiation loss and the steel shell would become appreciably hotter, but with 2½ in. of clay bricks laid on ½ in. of grog, the radiation losses should be comparable with those of the 70 per cent. alumina liner.

Other Methods of Removing Fire-Ring Slag.—It not infrequently happens that fire rings stop a kiln operating. One method of removal is the so-called water bar. When the obstruction is rather deep in the kiln, this system requires much room, many men, is clumsy of operation, and is bound to shorten the life of the lining. In other cases the rings are shot out with shells. At some plants, where the problem is especially acute, it is customary to add sand to the feed occasionally. The excess silica is instrumental in removing the rings, but it also tends to remove the coating, so that the lining is then subject to the direct abrasion of the charge with the result that its life is reduced. Serious product contamination also results from such a scheme. In the sintering of ore fines, blastfurnace flue dust, and similar materials European operators have developed a very stout water-cooled boring bar which enters the kiln through the hood, and, with a scraper arrangement, cuts the crust from the lining without interfering with the operation of the kiln. It may be, in order to obtain relief, that something similar to this will have to be developed for slag removal in lime kilns.

Coal.—Pulverised coal in suspension is an excellent fuel, meeting many of the variable requirements for the calcining of lime, but challenges the resourcefulness of most operators. Coal ash is the heaviest contributor to the rotary-kiln operator's difficulties. The theorist likes to think about burning lime at temperatures under 2,000 deg. F., but economic conditions make it necessary to use such fuels as are at hand. Certain advantages can be claimed for high-volatile versus low-volatile coal, or *vice versa*, but accessibility to either may be an important factor. It seems to resolve itself into the ability to modify the explosive tendency of finely-divided coal. If this is possible, flame temperatures will be held on the safe side of the ash-fusion point, and fire rings will probably disappear. Many operators will do well to study the quantity of air being used to dry the coal and get it out of the mill; the percentage will probably surprise them. Much in the way of flame-temperature modification can be accomplished by working toward the irreducible minimum, which should be about 12 per cent. Also, the admission of the preheated secondary air at a point 25 ft. or 30 ft. from the discharge end of the kiln should modify and lengthen the burning action. Another theory suggests the determination of the amount of coal ash entering the kiln per minute and the exact weight of the dust entering via the primary and secondary air. When these quantities are known, enough limestone can be added to the coal just ahead of the unit pulveriser to neutralise this and produce an ash content having a fusing point above that of the highest temperature attained in the burning zone of the kiln. Theoretically this will succeed; actually it will fail in part, because it is impossible to get the limestone into sufficiently intimate contact with all the low-fusing dust particles and keep the contact until they have passed on to the mass of material being burned, or to a point beyond which they would fuse.

In addition to the ring-forming characteristics of coal ash, some complaint is heard concerning the discoloration of the lime by a deposition of ash. A particle

of lime and adhering stain is first heated to a high temperature on the assumption that, if the stain were carbonaceous, the carbon will be burned off and the discoloration disappear. On this test the blackening disappears but a typical red ferric oxide (Fe_2O_3) scale remains. This indicates that the stain is ferrous oxide (FeO), which would be expected in a highly reducing atmosphere in a kiln and which, when further heated in the atmosphere, changes to the more stable compound Fe_2O_3. It is probable that the formation in the hot zone is almost pure-iron, and as it passes into the cooler zone it takes on a thin coating of FeO which gives the formation a blackish colour. Upon dissolving the particle in dilute hydrochloric acid the typical ferric-chloride colour develops and its essential nature is further confirmed by potassium thiocyanate and ferri-cyanide tests, each of which is highly sensitive and specific. Larger pieces of the quicklime are then selected and the scale scraped off with care to remove as little as possible of the underlying lime. By this means a relatively high concentration of the material is secured. The thiocyanate and ferri-cyanide tests are repeated and very strong shades of the characteristic colours develop. The precaution is observed of similarly treating equal quantities of the clean lime just under the scale thus removed, in order that assurance can be had that the slight iron content of the lime is not responsible for the colour reactions. It is entirely probable that the scale contains certain amounts of the other minerals inherent in coal ash, but it is certain that the black or brownish colour is entirely due to iron.

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Thermal Coefficient of Expansion of Portland Cement.

As the result of tests extending over a long period, Mr. S. L. Meyers, of the Southwestern Portland Cement Company (U.S.A.), has come to the following conclusions. The thermal coefficient of expansion appears to increase with the theoretical quantity of cement gel present if the cement gel is neither desiccated nor saturated with water. The coefficient decreases after long periods of time as the cement gel becomes a metacolloid ; any condition which accelerates this process decreases the coefficient. Neat Portland cement and concrete have lower coefficients under the conditions of water storage, steam treatment, and very dry storage, than under conditions of storage without gain or loss of water. The thermal coefficients of the four cement compounds are affected by storage conditions involving changes in humidity in the following order : tricalcium silicate, tetracalcium aluminoferrite, dicalcium silicate, tricalcium aluminate. The latter is affected very little or not at all. Since the thermal coefficients of different concretes vary over a wide range under different storage conditions as well as with the kind of concrete made, this variation should receive some consideration in the design of concrete structures.

The tests are described in *Industrial and Engineering Chemistry* for August, 1940, from which the following is taken.

The small amount of published research on the thermal coefficient of expansion of Portland cement and concrete contains many conflicting data. Regardless of kind of mix, type of Portland cement, or storage conditions of concrete, engineers usually use an approximate coefficient of thermal expansion—namely, 0·0000055 per deg. F. One reason for this unsatisfactory state of knowledge is the number of other volumetric movements in concrete that may occur simultaneously with thermal volume changes and vitiate the results. Some of these changes of volume are creep or flow of concrete under sustained loads, elastic or instantaneous changes under load, expansion in more humid conditions and contraction in less humid conditions, autogenous shrinkage or spontaneous contraction of gel structure, and chemical reactions such as hydration or sulphation of cement compounds and oxides.

Creep and elastic movements can be eliminated in controlled laboratory conditions. Autogenous shrinkage over the time of test is probably small, but changes in volume due to loss of water from test pieces to air are relatively great, and the specimens must be either in an atmosphere of controlled humidity or enclosed in airtight containers which do not restrict the movements of the specimens.

Test Procedure.

The method of making tests was described in a previous article[11] :

The test specimens were 1 in. in cross section and 13·5 in. long, with polished brass measuring studs cast in each end. The surface was made airtight by soldering paper-like copper foil jackets around the specimens. The bars were

tested for air leaks by blowing air into the copper jackets while they were immersed under water. A small copper tube was cast in the specimen; this could be filled with mercury and used as a thermometer well to take the temperature of the specimen in case there was any doubt of its having reached the temperature of its surroundings.

Changes in length were measured by an Invar micrometer having a very small but calibrated thermal coefficient. Most of the length-change tests were made between 70 deg. F. and 120 deg. F., and several hours usually elapsed before the bars came to equilibrium with the surrounding temperature. To compensate for any volume changes due to hydration during this period, the average change in length of the specimen during both a rising and falling temperature was used; if both periods of time were equal, the changes in length as reflected in the coefficient would cancel each other. With the exception of comparatively new specimens or specimens whose storage condition had recently been changed, the cycle from low to high temperature and then back to low temperature effected practically no measurable change in length for this time interval.

In most cases the neat specimens were mixed with water contents corresponding to normal consistency; they were stored in moulds for 24 hours or until strong enough to handle, and then sealed in the impermeable jackets. Some water was lost during this stage. During normal enclosed air storage there would be no gain or loss of moisture (no change in weight) if the sealed covering were perfect; this was not always the case since frequent tests showed some small leaks at times. This was a small factor in decreasing the water content of the specimens with time; a major factor would be the absorption of free water to hydrate the anhydrous cement compound and the possible change of free water to the form of "sorbed" or physically-bound water.

In water storage, water was placed within the flexible copper foil covering; some of the water was absorbed by the specimens, but sufficient water was present so that the mortar surfaces of the specimens were always covered with free or mobile water.

Drying storage was obtained by circulating room air through the space between the specimen and the jacket; at times air in equilibrium with moderate vapour pressure salts such as ferrous sulphate, calcium chloride, barium chloride, etc., was used for drying.

For extreme drying or a desiccating condition, air in equilibrium with quicklime or phosphorus pentoxide was circulated around the specimens, or they were placed in a vacuum at room temperature. In the case of oven drying they were exposed to the air without covers at 100 deg. C.

One of the objects of making this study was to see if there was a relation between the thermal coefficient and the chemical or compound composition of the cement. Results up to about one year indicated that the coefficient followed the amount of tricalcium silicate in the cements; those high in this compound had a high coefficient; conversely, those low in tricalcium silicate had a low change of volume with temperature change.[11] Later results indicated that this

was true only for early ages, and in time cements low in tricalcium silicate appeared to have a coefficient in the same range as high tricalcium silicate cements.

Theory of Gel Structure and Cement Properties.

The thermal expansion behaviour seems to be generally consonant with a new view that high coefficients are associated with theoretically large quantities of cement gel containing a medium amount of water, and low coefficients are associated with a theoretical low gel content, a desiccated, aged, or hardened gel, and a water-saturated gel.

To understand the relation between the test results given here and the gel structure of hardened water-gauged Portland cement, a brief outline of the composition and hydration of Portland cement is given in *Table* I. Both crystalline and colloidal materials are shown to be present in hydrated Portland cement ;

TABLE I

COMPOSITION AND HYDRATION OF PORTLAND CEMENT

Principal Compounds in Cement Clinker	Hydrated Chemical Products When Mixed with Water to Paste Consistency	Reaction Rate of Anhydrous Particles with Water, and Depth of Reaction at Surface (*1*) in Microns	% Fixed Water Retained after Drying at 105° C. (*8*)		Physical State of Hydrated Reaction Products from Hardened Cement Pastes (*15*)
			7 days	2 years	
Tricalcium silicate, $3CaO.SiO_2$ (C_3S)	$2CaO.SiO_2.xH_2O + Ca(OH)_2$	Rapid; 1.68 at 3 hr., 4.44 at 28 days	12 0	18 6	Colloidal $2CaO.SiO_2.xH_2O$ and fine crystals of $Ca(OH)_2$ embedded in silicate gel; gel surrounds anhydrous grain centers
Dicalcium silicate, $2CaO.SiO_2$ (C_2S)	$2CaO.SiO_2.xH_2O$	Very slow; 0.83 at 28 days	1 7	12 1	Colloidal $2CaO.SiO_2.xH_2O$; gel surrounds anhydrous grains; no $Ca(OH)_2$ crystals
Tricalcium aluminate, $3CaO.Al_2O_3$ (C_3A)	$3CaO.Al_2O_3.xH_2O$	Very rapid; 4.35 at 3 hr., 5.66 at 28 days	32 4	38 5	Fine crystals of $3CaO.Al_2O_3.xH_2O$; either temp. or time will convert to stable $3CaO.Al_2O_3.6H_2O$
Tetracalcium aluminoferrite, $4CaO.Al_2O_3.Fe_2O_3$ (C_4AF)	$3CaO.Al_2O_3.xH_2O + CaO.Fe_2O_3$	More rapid than C_2S but not so rapid as C_3A	27.1	30 1	Fine crystals of $3CaO.Al_2O_3.xH_2O$ and amorphous $CaO.Fe_2O_3$; colloidal gel of calcium ferrite surrounds anhydrous grain centers; hydrated tricalcium aluminate crystals fill adjacent voids; some later decompn. of $CaO.Fe_2O_3$ into $Ca(OH)_2$ and Fe_2O_3

but since the silicates which form the silicate gel predominate, and the crystalline lime split off during the hydration of C_3S is not effective as a cementing agent, it is now generally agreed that the properties of hydrated Portland cement are closely connected with its colloidal structure.

Many minerals are formed in nature as colloids or amorphous materials, and in the course of time they change to crystalline minerals. Only a limited number of compounds has the property of enduring as gels for a long time ; the majority soon become crystalline, which is the stable condition of minerals in nature. The transformation from gels to crystals is spontaneous, but its rate can be accelerated by changes in its environment, such as temperature and humidity, and by shock, pressure, and loss of water to water-abstracting salts.

In changing to a crystalline state, hydrous silica gel passes through the following stages : silica gel, opal and its varieties, cacholong, chalcedony, and finally quartz. Each step in this transition is accompanied by water loss, starting with a high water-content gel and ending with anhydrous quartz.[4]

Many investigators have used silica gel as an analogy to explain the properties of hydrated Portland cement. Some of the properties of hydrated cement that place it in the colloidal class are as follows : Expansion and contraction due to wetting and drying[17] ; the fact that the volume of hydrated cement is less than

the original volume of anhydrous cement plus water[8]; plasticity and viscosity of wet cement pastes[16]; adhesion, binding power, and mechanical strength[5]; selective absorption[9]; effect of electrolytes in causing variation of set[13]; heat of surface wetting[12]; impermeability[6]; variations in such mechanical properties as plastic flow, Young's modulus, and thermal coefficient of expansion.[10]

Cement particles hydrated with a great excess of water show much crystal growth; but in water concentrations of mortar and concrete consistencies only amorphous products are easily discernible. Many years ago Kühl studied, under the microscope, fresh cement pats made of pastes ranging from 25 to 70 per cent. of water to weight of cement, but could find no evidence of crystals; twenty years later the same specimens were re-examined and showed some crystallinity under the polarising microscope, and those pastes which had been mixed with the greatest percentages of water showed most crystal development.

Water contained in hardened Portland cement pastes may be arbitrarily divided into three classes: (1) Free or mobile water in the macropores, which will evaporate into air spaces at a vapour pressure just below that of water. (2) Mechanically held water, either as part of the gel structure, entrained in capillaries, or adsorbed to gel, crystal, or other substances. The more loosely held mechanical water is easily evaporable; the more firmly held, as that in the smallest capillaries, will not evaporate at vapour pressures approaching zero. (3) Water held chemically as hydrates, often found as part of a definite crystal structure losing water at a definite temperature.

Hydrated Portland cement, then, contains colloidal gel-like material that probably passes through similar stages to that of inorganic colloidal minerals in nature with time—that is, from expanded gels with high water contents to desiccated and relatively inert metacolloids and possibly further, if sufficient time is allowed, to all-crystalline compounds. The following test results indicate that the property of thermal expansion of hydrated Portland cement is greatly affected by the theoretical quantity of gel present and its condition of humidity or possibly vapour pressure.

Test Results on High and Low Tricalcium Cements.

In *Fig.* 1 the thermal coefficient rises rapidly in the high C_3S cement, reaches a maximum at about five months, and then drops off. In this cement rapid hydration has developed much gel in the early periods; and the ageing of this gel into a metacolloid, possibly accompanied by the progress of crystallisation of those substances approaching the amorphous state, has lowered the coefficient.

In the case of the low C_3S cement, less gel is formed in the early stages and the coefficient reaches its maximum at a later period. Accordingly the ageing of the gel starts later and the coefficient falls later, but is somewhat above the coefficient of the higher C_3S cement, possibly because a small amount of fresh gel is still being formed from the slow-hydrating constituents which to a small degree offsets the effect of the ageing of the gel previously formed.

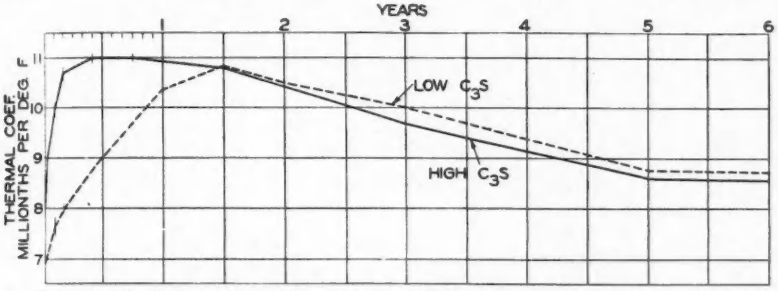
The fall of the coefficient at later ages may not be due to gel ageing alone; in spite of being sealed in airtight containers, leaks in the envelopes did occur,

resulting in some drying out which would also lower the coefficient if the drying approached a condition of desiccation.

Some investigators have previously indicated a connection between age and thermal coefficient. Rudeloff and Sieglerschmidt stated that the coefficient of expansion increases with age ; they even found a negative coefficient for early-age water-stored specimens.[14] The concrete tests of Hatt showed lower coefficients at two months wet than at four months dry.[7] Davis and Troxell reported that age had practically no effect on the coefficient.[3]

Thermal Coefficient of Concrete.

Fig. 2 shows the effect of time on the coefficient of concrete bars where different aggregate is used. Except where noted in the caption, all concrete was made as follows : Mix 1 : 4·7 ; fineness modulus 4·01 ; consistency about equivalent to a 1-in. slump ; normal Portland cement. The age curves are about the



Cements mixed neat at normal consistency and stored in enclosed air-sealed jackets ; compound compositions as follows :

	Average of 9 High-C_3S Cements, per cent.	Average of 4 Low-C_3S Cements, per cent.
C_4AF	9·11	6·78
C_3A	8·59	4·10
C_2S	9·12	46·45
C_3S	66·82	35·60

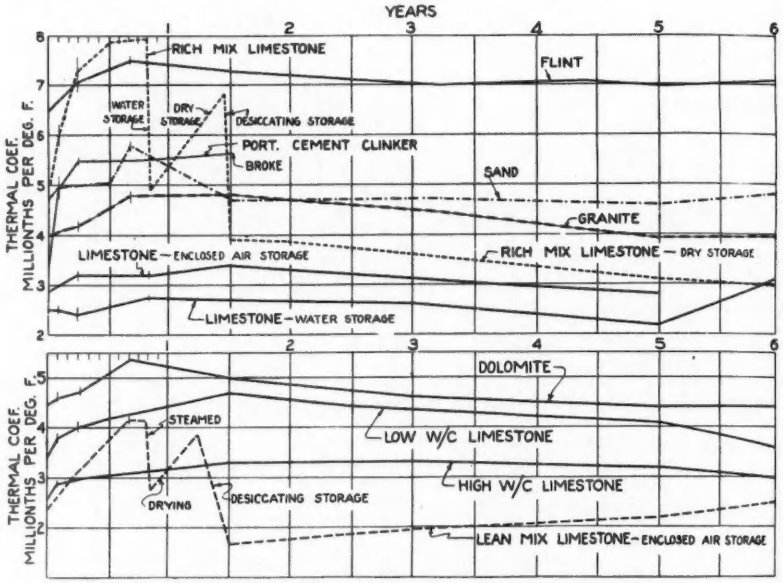
Fig. 1.—Comparison of High and Low Tricalcium Silicate (C_3S) Cements for Thermal Expansion.

same general shape for concrete as for neat cements. The coefficients are lower, but any change of coefficient with time is probably due to changes within the cement paste part of the concrete and not to the aggregate. The coefficient of the bar made with Portland cement clinker gives some indication of what the unhydrated centres of clinker grains contribute to the coefficient of expansion of a hardened cement paste. In the same way as with hardened neat cements but to a lesser degree, the coefficient of either water-saturated or of desiccated gel concrete is lower than when the gel is expanded but not saturated with water.

It might be objected with some force that where the storage conditions are changed to extremes, back and forth, and where the specimens undergo a temperature cycle with each test, it is difficult to evaluate the effect of age alone.

Yet with the exception of vacuum storage and extreme drying, similar conditions prevail in structural concrete exposed to the elements; but because of the differences in size the change will not be as abrupt as in the small specimens used in this test.

In *Fig.* 2 sharp changes of direction are given because measurements were taken at these points. Had measurements been taken continuously, the shape of the curves would have been rounded and the changes in direction with continued drying would have been easier to understand.



Mix, 1 : 4·7, except for the rich limestone mix (upper figure) which was 1 : 3·1, and lean mix concrete (lower figure) which was 1 : 7·5. Enclosed sealed air storage, except for rich mix limestone and limestone stored in water, and for a part of the storage time of lean mix concrete. Aggregates graded from 100 mesh to ¼-in., fineness modulus 4·01. Consistency equivalent to a 1-in. slump, except for high water-cement ratio concrete which was about 7-in. slump and low water-cement ratio concrete which had practically no slump.

Fig. 2.—Thermal Coefficient of Expansion of Concrete.

Table II shows the degree of lowering of the coefficient by saturating cement or concrete bars with water. Extreme drying (*Table* III) has the same effect as age in desiccating and hardening the gel structure. Absorption of moisture after drying by creating fresh gel may again raise the coefficient.

The results in *Table* IV indicate that storage in liquids such as kerosene and glycerol have practically no effect on the thermal coefficient, as does water. There was no expansion or contraction of the bars at constant temperatures while stored in kerosene or glycerol, which indicates that these liquids do not become integral parts of the cement gel structures as does water.

Table V gives the effect on nine cements, containing both high and low C_3S cements, of steam treatment with enclosed covers for 24 hours at 205 deg. F. After steaming, enclosed air storage was used to the end of the test. Results are also given for one bar autoclaved at 500 deg. F. for two weeks.

Steam treatment lowers the coefficient, but it may be due either to ageing of gel structure or the presence of excess moisture as in water storage. Mild steaming does not completely hydrate the cement, and later hydration forms new gel with a rise of coefficient. This did not occur to the same extent in the bar more

TABLE II. EFFECT OF SATURATION WITH WATER ON THERMAL COEFFICIENT

Type of Bar	Thermal Coefficient: At age of 9 mo. before satn.	Thermal Coefficient: After soaking in water 1 week
Portland-lime masonry cement	0.0000104	0.0000053
Normal portland cement	0.0000103	0.0000057
Flint concrete	0.0000081	0.0000049
1 cement:1 sand mortar	0.0000092	0.0000063
High tricalcium silicate cement	0.0000114	0.0000056

TABLE III. EFFECT OF EXTREME DRYING OR DESICCATION ON THERMAL COEFFICIENT

Type of Bar	Thermal Coefficient: Before drying	Thermal Coefficient: After drying 1 week at 100° C. without covers	Thermal Coefficient: After several years in enclosed air storage
High early-strength cement	0.0000091	0.0000060	.....
White cement	0.0000104	0.0000065	0 0000067
Normal portland cement	0.0000094	0.0000060	0 0000067
Portland-lime masonry cement	0.0000080	0.0000037	.....
Limestone concrete	0 0000041	0.0000021	0 0000?22
Plastic portland cement	0.0000100	0.0000059	.....

TABLE IV. EFFECT OF KEROSENE AND GLYCEROL STORAGE ON THE THERMAL COEFFICIENT OF NEAT CEMENT BARS

Kind of Bar	Thermal Coefficient: Before soaking	Thermal Coefficient: After soaking in kerosene 4 mo.	Thermal Coefficient: After soaking in glycerol 3 yr.
Normal portland cement	0.0000106	0.0000108	0.0000100
Flint concrete	0.0000076	0.0000072	0.0000072
Clinker, no gypsum	0.0000112	0.0000114	0.0000101
Cement from slow cooled clinker	0.0000119	0.0000112	0.0000105
High C_3S cement	0.0000106	0.0000116	0.0000118*

* After 7 months.

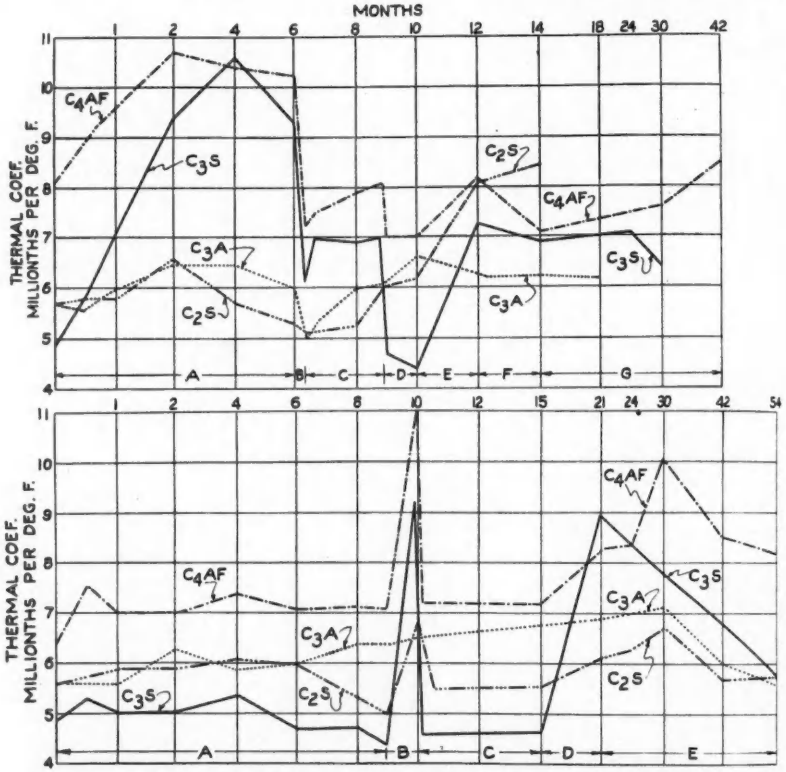
TABLE V. EFFECT OF STEAMING ON THERMAL COEFFICIENT

	Age 5 Weeks before Steaming	After Steaming	6 Mo. after Steaming	1 Yr. 2 Mo. after Steaming	4 Yr. 4 Mo. after Steaming
Av. for 9 cements	0.0000076	0.0000059	0.0000069	0.0000087	0.0000084
Bar autoclaved 2 weeks at 500° F.	0.0000096	0.0000053	0.0000056	0.0000069	0.0000056

completely hydrated at 500 deg. F. for two weeks, since this treatment probably hydrated all of the dicalcium silicate. Since only one test bar was subjected to the 500 deg. F. test, the results should be accepted with caution.

The one point of agreement of nearly all published results on the thermal coefficient is that it increases with richness of mix; average results on four mixes, up to two years, are as follows: Neat normal cement, 0·0000103; 1 cement : 1 sand, 0·0000075; 1 cement : 3 sand, 0·0000062; 1 cement : 6 sand, 0·0000056.

Fig. 3 shows the thermal coefficient of expansion for the four compounds common to Portland cement clinker under different moisture conditions. Three of these compounds—C_3S, C_2S, and C_3A—were furnished by Mr. R. H. Bogue. The fourth, C_4AF, was prepared here. All four samples were ground in a hand mortar, and the resulting low-flour products were mixed with the following



Upper graphs.—*A*, normal or enclosed air storage. *B*, stored in vacuum over quicklime. *C*, stored in circulating enclosed moist air. *D*, water storage. *E*, stored in enclosed moist air. *F*, stored in enclosed air in equilibrium with Epsom salts, vapour pressure 4·9 mm. *G*, stored in circulating enclosed air in equilibrium with $CaCl_2$, vapour pressure 5·1 mm. and above.

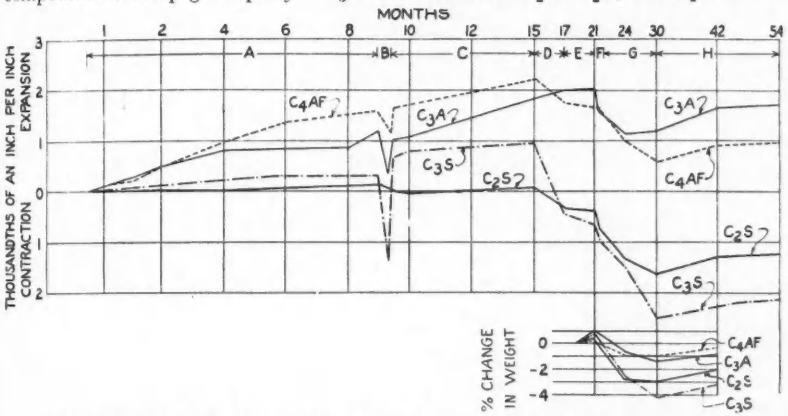
Lower graphs.—*A*, *C*, water storage. *B*, *D*, enclosed circulating dry air. *E*, normal enclosed air storage.

Fig. 3.—Thermal Coefficient of Expansion of the Four Major Compounds in Portland Cement.

minimum amounts of water necessary to allow placing in the moulds (in per cent.): Tetracalcium aluminoferrite, 19·0; tricalcium aluminate, 33·1; dicalcium silicate, 29·0; tricalcium silicate, 31·0. Owing to the weakness of the C_3A and C_2S, tests did not start until after two weeks. The lines to the left of two weeks on *Fig.* 3 are extrapolated.

Two test pieces were made of each of the four individual compounds, one of each was placed in water storage, and one of each was kept sealed in flexible containers to prevent loss or gain of moisture ; this condition is meant by normal enclosed air storage. After several months the conditions of storage were reversed with some variations between the two groups. Each of the four specimens in the group starting with enclosed-air storage broke while handling before the end of the tests, which indicated that initial air storage may have made the specimens more brittle than initial water storage.

The C_3S and C_4AF both have high coefficients at a maximum ; both of these compounds develop gel rapidly. C_3S forms colloidal $C_2S.xH_2O$, and C_4AF forms



Measurements taken at constant temperature ; lower right-hand corner shows changes in weight of the same specimens.

A, water storage. *B*, low-humidity air. *C*, water storage. *D*, circulating air in equilibrium with $F_2SO_4.7H_2O$, vapour pressure 14·5. *E*, circulating air in equilibrium with $CaCl_2.6H_2O$, vapour pressure 5·1 mm. and above. *F*, circulating air in equilibrium with concentrated H_2SO_4, vapour pressure 0·20 mm. and above. *G*, stored in circulating air of low relative humidity. *H*, normal enclosed air storage.

Fig. 4.—Volume Changes Due to Other Than Thermal Changes in the Four Major Compounds in Portland Cement.

amorphous hydrated calcium ferrite. The C_3S appears to be more sensitive to water saturation and also to drying out than any of the other compounds, but C_4AF is next in this property.

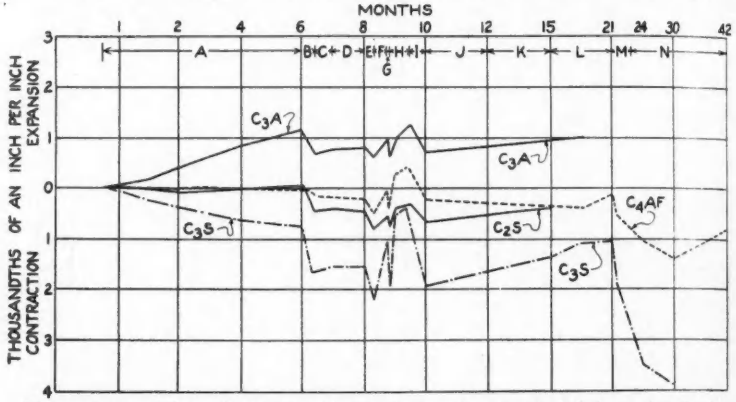
The C_2S, which hydrates slowly, shows a low coefficient with changing moisture storage until later ages, when more gel is formed ; even then it does not approach C_3S or C_4AF in sensitiveness to storage changes. The C_3A hydrates rapidly, but its products are crystalline, and therefore show a continuously low coefficient and lack of sensitiveness to storage conditions.

Figs. 4 and 5 give volume changes due to other causes than thermal changes, the principal cause probably being moisture changes ; all measurements were taken at a constant temperature.

Contrary to other investigators' results, the C_3A and C_4AF did not shrink in air as much as was to be expected. This may be due to the small amount of

mixing water used (about 10 per cent. below the hydration requirements in each case). The low-water-content pastes would give an initially compact structure; and the further taking up of needed water, which could occur even in air, would expand the hardened mortar.

In the lower right-hand corner of *Fig.* 4 some changes in weight which accompanied the volume changes are shown; they were not started until later ages and



Measurements taken at constant temperature; storage started in enclosed air. *A*, *D*, *J*, *N*, normal enclosed air. *B*, stored in vacuum over quicklime. *C*, *E*, circulating air with average relative humidity of 40. *F*, circulating moist air. *G*, circulating air with very low relative humidity. *H*, water storage. *I*, circulating air with low relative humidity. *K*, circulating air in equilibrium with Epsom salts. *L*, circulating air in equilibrium with $CaCl_2$, vapour pressure 5·1 mm. and above. *M*, circulating air in equilibrium with concentrated H_2SO_4, vapour pressure 0·20 mm. and above.

Fig. 5.—Volume Changes Due to Other Than Thermal Changes.

so are incomplete, but gains in weight generally correspond to increase in length and loss of weight to decrease in length. However, there can be shrinkage without a loss in weight, and this appears to be due to autogenous shrinking of the gel present, one of the concomitants of gel ageing.

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